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A Review on the Preparation and Characterisation of ZnO Thin Films by Chemical Bath Deposition Method

V. Radhika[*] and V. Annamalai[**]

[*]Assistant Professor, Department of Physics,
PKR Arts College for Women, Gobi, INDIA.
[**]Assistant Professor, Department of Physics,
Chikkanna Govt. Arts College, Tiruppur, INDIA.
email:radhikaviswanath@gmail.com, annamalai_14075@yahoo.co.in

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ABSTRACT

As a II–VI semiconductor, zinc oxide (ZnO) has a wide band gap (3.3 eV), large exciton binding energy and has wide applications in various fields such as transducers, gas sensors, and surface acoustic wave devices. ZnO thin films prepared by different coating techniques can possess high electrical conductivity and high visible transmittance. Various chemical and physical deposition methods have been applied to fabricate ZnO thin films. In most cases, high temperature and special atmosphere are necessary. But the chemical bath deposition (CBD) method represents a simple and effective way of deposition. Basically, CBD processes involve preparing ZnO nanoparticles seed layer on special substrate, usually using sol–gel method, and treatment of seeded substrate in a solution that contains Zn^{2+} and precipitation agents[1]. The different methods of preparation of ZnO thin films on glass substrates by CBD method and some of their properties are briefly discussed.

Keywords: ZnO nanoparticles, CBD method, Chemical bath, thin films.

INTRODUCTION

Presently, various chemical and physical deposition methods have been applied to fabricate ZnO thin films. For instance, metal-organic chemical vapor deposition (MOCVD), a vapor–liquid–solid mechanism, pulsed laser deposition, spray

pyrolysis, sol–gel, and radiofrequency magnetron sputtering are in use. Among these, (i) CBD method and (ii) the Successive Ionic Layer Adsorption and Reaction (SILAR) technique are discussed here. The CBD method represents a simple and effective route. Chemical bath deposition (CBD) was used for the preparation of semiconducting oxide films. CBD is known to be a simple, low temperature and inexpensive large-area deposition technique[5]. The film surface is with a ganglia-like structure as observed by Scanning Electron Microscopy (SEM)[3]. The films comprise of ZnO nanocrystallites with hexagonal crystal structure, as revealed by means of X-ray diffraction (XRD).

Zinc oxide (ZnO) thin films were also grown on glass substrates by the SILAR technique. In this technique, a glass substrate is dipped alternatively into beakers containing aqueous solutions or distilled water for the reaction to take place at the substrate surface. The factors affecting the process are the quality of the precursor solutions, their concentrations, pH values, complexing agents and individual rinsing and immersion time periods[2]. The crystal structure can be compared from their respective XRD patterns. The optical characteristics of the samples were obtained by using UV-Visible spectrophotometer at 200–900 nm wavelengths. The optical constants (refractive index, extinction coefficient etc.) of the ZnO thin films depend on preparation conditions[7].

The aim of this paper is to compare the preparation methods and some optical properties like absorbance and transmittance of ZnO thin films obtained on glass substrate.

EXPERIMENTAL PROCEDURE

Preparation of ZnO Thin Film:

Dewei Chu *et al.*[1], observed that ZnO films were grown using a simple two-step process: (1) spin-coating ZnO seeds on the substrate and growth of films on the seeded substrate. The ZnO seed was prepared by a modified sol–gel method. 0.09 g $Zn(CH_3COOH)_2$ and 0.12 g KOH were dissolved into 50 ml methanol, respectively. They were mixed rapidly, and stirring at 60°C for 5 min, then cooled to room temperature. The resultant solution was transparent with ZnO particles. The solution was then spin-coated on the substrate at 500 rpm for 5 s, and 3000 rpm for 30 s. After processing, the substrate was heated at 60 °C for 10 min to remove the solvent. (2) The ZnO growth was carried out by suspending the substrate in a 40 ml beaker filled with an equimolar aqueous solution of zinc nitrate hydrate and monoethnolamine at 90 °C for 1 h. Subsequently, the substrate was removed from the solution, rinsed with deionized water and dried in air at 60 °C. The phase composition of the samples was characterized by X-ray powder diffraction.

A. Raidou *et al.*[2], reported as follows. Zinc oxide (ZnO) thin films were grown on glass substrates by the SILAR technique which is mainly based on the adsorption and reaction of the ions from the solution. To avoid homogeneous precipitation in the solution, the substrate is rinsed with deionised water between every immersion. ZnO films are obtained by successive immersion of a substrate in this aqueous solution. 100 ml of zinc sulfate and 6ml/100ml 13.15 M aqueous ammonia solution as precursor solution is taken. The pH was adjusted by KOH addition.

In the first step, the substrate was immersed in a beaker containing $Zn(SO_4)$ and ammonia solution, where Zn^{2+} with ammonia formed zinc ammonia complex ($[Zn(NH_3)_4]^{2+}$). In the first immersion process, zinc ammonia was adsorbed onto the substrate. In the second step, the zinc ammonia adsorbed substrate was immersed into beaker containing the distilled water, where the adsorbed zinc ammonia complex was converted into zinc hydroxide ($Zn(OH)_2$). Each immersion step took a time period of 30 s.

N. V. Kaneva *et al*.[3], reported that the nanocrystalline ZnO thin films were deposited from sol-gel method (Fig. 1) using dip coating onto glass substrate. The sol was obtained using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), 2-methoxyethanol and monoethanolamine, mixed together in a round-bottomed flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60 °C upon magnetic stirring for 60 min and let overnight. The obtained sol was clear and homogeneous to serve as the coating substance for film preparation. Dipping the glass substrate in the sol and withdrawing it at a rate of 0.9 cm/min at room temperature prepared the gel films. A higher withdrawal rate results in films of lower quality. The films were deposited with 5 coatings and dried at 80 °C for 15 min after each successive coating. The final gel films onto glass substrate were annealed at 500 °C for 60 min in order to obtain the ZnO films.

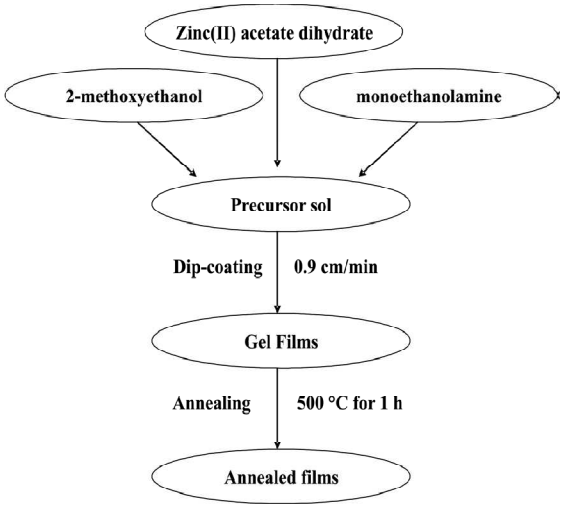

Fig. 1[3]. Scheme of the experimental procedure for deposition of thin ZnO films by sol-gel dip coating[3]

S Mondal and P Mitra[4] deposited ZnO from 0·1M sodium zincate (Na_2ZnO_2) solution and hot water bath. The sodium zincate bath used for deposition was prepared by adding sodium hydroxide (NaOH pellets, mol. wt 40·00) in zinc sulphate ($ZnSO4{\cdot}7H_2O$, mol.wt 287·54) solution. pH of the zincate solution was 13·20. pH measurement was carried out in a pH meter.

Mohammad M. Ali[5] prepared ZnO films using aqueous solutions of $Zn(CH_3COO)_2.2H_2O$, triethanolamine (TEA) and NaOH in de-ionized water to the volume of 100ml. The substrate was cleaned with toothpaste (because it is a mild abrasive, then washed in warm soapy water and a water-ethanol (50:50) solution) and then dried. Prior to the deposition, the beaker containing the deposition solution was placed in the water bath at 80 ^oC for about 5 minutes to stabilize the temperature of the solution, and then the beaker was kept in the water bath. At the end of the deposition time (˜ 2.15 hours), the slides were taken out, rinsed with distilled water and allowed to dry with warm air. The slides were observed to have been coated with milky white deposits. The equation of the reaction is shown below:

$Zn(CH_3COO)_2.2H_2O + TEA \rightarrow [Zn(TEA)]^{2+} + 2CH3COO^- [Zn(TEA)]^{2+} \rightarrow Zn^{2+} + TEA$

$2NaOH \rightarrow 2Na^+ + 2OH^-$

$Zn^{2+} + 2OH \rightarrow Zn(OH)_2 \downarrow$

$Zn(OH)_2 \rightarrow ZnO + H_2O \uparrow$

They were later annealed at different temperature (300^{o}C, 350^{o}C and 400^{o}C) for 12 minutes.

Ezenwa I.A.[8] reports the synthesis of zinc oxide (ZnO) thin film using the electroless deposition method based on the reaction between zinc acetate (Zn(CH3COO)2 and sodium hydroxide (NaOH), using Ethylene diamine tetraacetate (EDTA) disodium salt -(OOCCH2)2 N-CH2-CH2-N (CH2COO)2– 2Na+ .2H2O as a complexing agent.[8] EDTA disodium salt is used to eliminate spontaneous precipitation of the chemical reagents and ensure ion by ion condensation. Details of bath constituents for the synthesis of ZnO thin films are shown in table 2.

Table-2

Bath constituents for synthesis of ZnO *Slide* No.	**1M $Zn(CH_3(00)_2$ Vol. (ml)**	**1M NaOH Vol. (ml)**	**1M ED.T. A Disodium Vol. (ml)**	**Dip time (hrs)**
ZnO1	10.00	10.00	0.50	24.00
ZnO2	10.00	10.00	1.50	24.00
ZnO3	10.00	10.00	2.50	24.00
ZnO4	10.00	10.00	3.50	24.00
ZnO5	10.00	10.00	4.50	24.00

RESULTS AND DISCUSSIONS

Optical properties:

A. Raidou *et al*.[2], observed that with increase in bath temperature, the transmittance decreases. Fig. 3[2] shows the transmittance and absorbance spectra of ZnO thin films deposited at different bath temperatures 75 °C, 80 °C and 85 °C. The spectra showed that the ZnO films have low absorbance in the visible region. The transmittance edge was seen to be shifted slightly towards higher wavelength as the

bath temperature was increased. This shift indicates decrease in band gap, which can be attributed to increase in the thickness and in grain size with bath temperature. Also Fig. 3(a) shows the occurrence of peaks in the absorbance (transmittance) plot at 358 nm. These peaks are attributed to the formation of excitons in ZnO thin films, by bath temperature, which decreased with decreasing the bath temperature. This last parameter influences a shift between the spectra, which means the decrease of band gap energy[2].

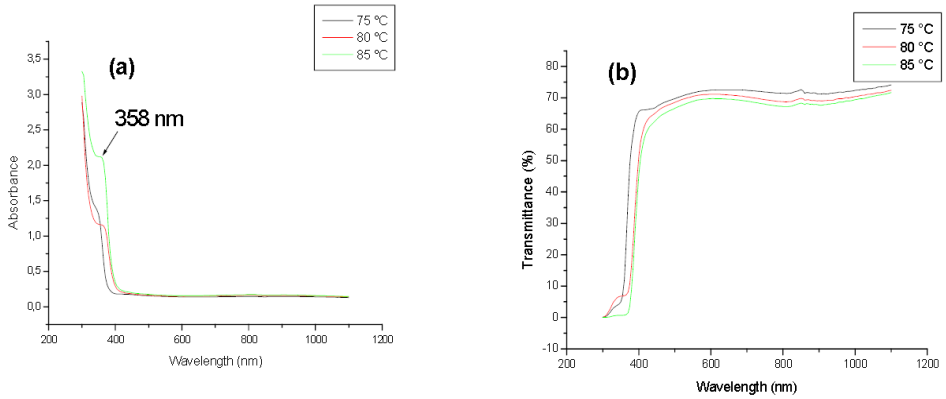

Fig.2 Absorbance and Transmittance spectra of ZnO thin films deposited in the same conditions and at different temperatures T = 75°C, 80°C

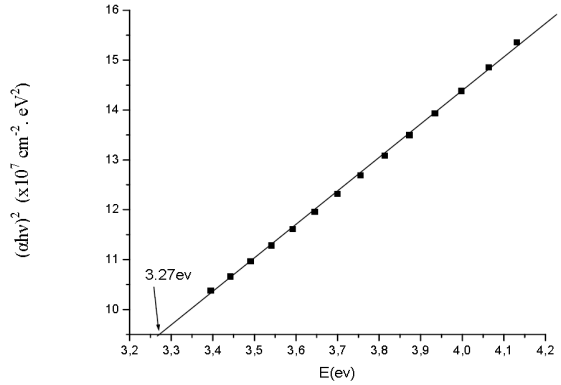

Fig.3 Determination of the band gap of a ZnO thin film deposited on glass substances from a basic solution (pH = 10.47), immersion time: 30s, number of cycles 20 and bath temperature 80°C

The ZnO is a wurtzite structure semiconductor with direct band gap of 3.3 eV. The band gap was estimated using the Tauc's relationship between the absorption coefficient, α , and the photon energy, $h\upsilon$, using $\alpha h\upsilon = A(h\upsilon - E_g)^n$ where $n = 1/2$ for direct allowed transitions and $n = 2$ for allowed indirect transitions. This equation

gives the values of direct and indirect band gap (E_g), when straight portion of $(\alpha h\upsilon)^2$ against $h\alpha$ plot and $(\alpha h\upsilon)^{1/2}$ as plotted against $h\alpha$ plot, and extrapolated to $\alpha = 0$. Fig. 4 shows the linear part of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for ZnO film and the band gap was found to be 3.27 eV^2. The Optical absorbance spectra of the deposited ZnO films were obtained by means of spectrophotometer[8].

Figure - 5 shows the absorption spectrum in the wavelength range 300 - 1100 nm of ZnO thin film. It is found that the absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. A strong absorption of about 0.75 was observed at wavelength of 320nm, hence the film has potential application in fabrication of solar cell[8].

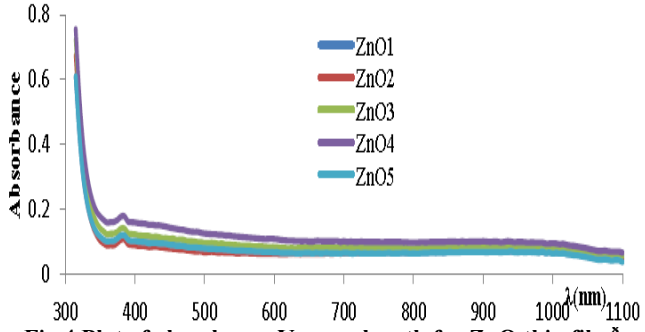

Fig.4 Plot of absorbance Vs wavelength for ZnO thin film[8]

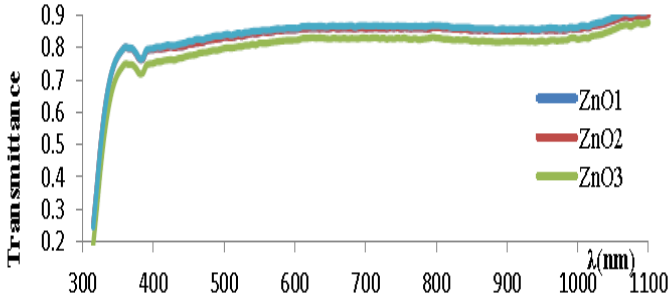

Fig.5 Plot of transmittance Vs wavelength for ZnO thin film[8]

The transmission spectra displayed in fig.6 shows that the films transmit well in the VIS / NIR region of the solar spectrum. The film's transmittance increases gradually with wavelength in the VIS region of the solar spectrum, with about 0.85 (85%) at wavelength range of 600nm–900nm[8].

Parameters such as transmittance, reflectance, refractive index and extinction coefficient were then calculated using the relationship explained below:

For weakly absorbing thin film on a non absorbing substrate, the transmittance

(T) can be expressed as[9] : $T = (1-R^2) \exp(-\alpha t)$, and $t = 1/\alpha \{\ln (1-R^2) / T\}$ where R is the reflectance, α is absorption coefficient, t is the thickness of the film.

Figure - 7 shows a plot of α^2 versus photon energy (hυ) of ZnO thin films. The energy gaps for these films are obtained by extrapolating the linear part of the curve to $\alpha^2=0$. This yielded a band gap of 3.00 eV for ZnO thin film[8]. The values of pH, refractive index, *n*, and extinction coefficient, *k*, at 550 nm wavelength, thickness, *d*, and band gap energy, E_g of the ZnO thin films prepared at different preparation routes and coating techniques[7] are tabulated.

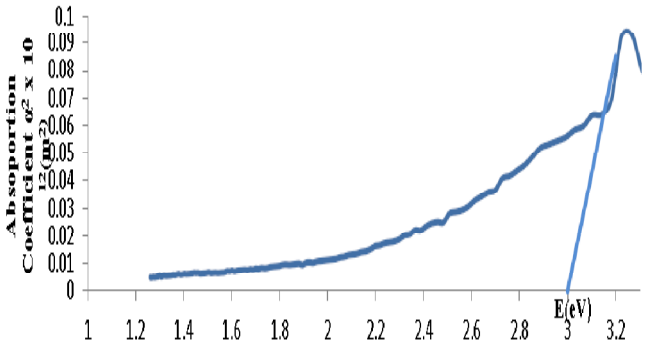

Fig.6 Plot of absorption coefficient squared Vs photon energy for ZnO thin film[8]

Sample	Technique	pH	*n*	*k*	*d* [nm]	*E*g [eV]	Morphology
S1	drainage	7.1	1.582	0.014	348	3.28	Porous
S2	Dip	6.5	1.591	0.015	312	3.11	Rough
S3	Dip	7.1	1.608	0.022	376	3.08	Microcrack
S4	Dip	6.8	1.623	0.013	358	3.27	Smooth

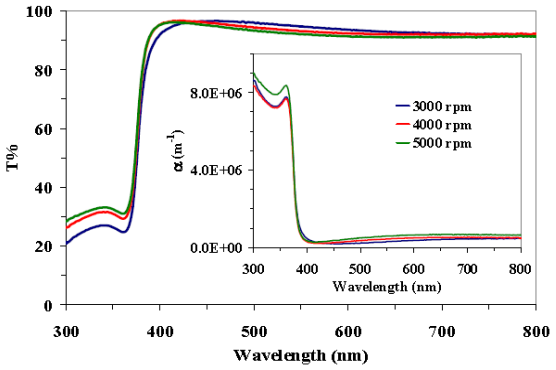

Fig.7 Optical transmittance and absorption coefficient spectra of ZnO thin films prepared by sol-gel spin coating method[13]

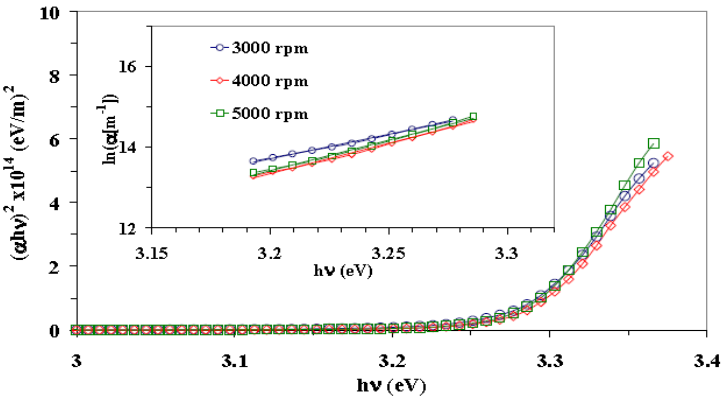

Fig 8. The plots of (αhυ)2 and ln(α) vs. photon energy of ZnO thin films[13] deposited by spin coating.

The optical transmittance and absorption coefficient spectra of the thin films in the UV–visible wavelength range are presented[13] in Fig.8.

It can be seen that the films have high transparency in the visible range (>92%)[13].

Fig. 9 shows plots of (αhυ) vs. *h*υ. *Eg* values change with chuck rotation rate. The chuck rotation rate is responsible for the width of localized states in the optical band of the films.[13]

CONCLUSIONS

Thus, the ZnO thin films could be successfully synthesized through the simple chemical bath techniques. The optical and morphological properties of the sol-gel derived ZnO thin films strongly depend on the preparation conditions[7]. The films may be characterized by means of scanning electron microscopy and X-ray diffraction: The films comprise ZnO crystallites with a hexagonal wurtzite structure[3]. The dip coated ZnO thin film using DEA as stabilizer for the sol exhibits better quality as the band edge transition peak is intense and the sub-band transition peak is suppressed[7]. The optical properties – transmittance, absorbance and absorption coefficients of ZnO thin films, coated differently are also discussed briefly.

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